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COMMUNICATION

The European Patent Office herewith transmits as an enclosure the European search report for the above-mentioned European patent application.

If applicable, copies of the documents cited in the European search report are attached.

☒ Additional set(s) of copies of the documents cited in the European search report is (are) enclosed as well.

The following specifications given by the applicant have been approved by the Search Division:

☒ abstract ☒ title

☐ The abstract was modified by the Search Division and the definitive text is attached to this communication.

The following figure will be published together with the abstract: 1

REFUND OF THE SEARCH FEE

If applicable under Article 10 Rules relating to fees, a separate communication from the Receiving Section on the refund of the search fee will be sent later.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 5260

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	FR 1 218 766 A (WOLFF & C° KOMMANDITGESELLSCHAFT AUF AKTIEN) 12 May 1960 (1960-05-12) * page 1, right-hand column, line 21 - line 25 * * page 2, left-hand column; example *	1-4	C08B1/06
A	CHEMICAL ABSTRACTS, vol. 127, no. 2, 14 July 1997 (1997-07-14) Columbus, Ohio, US; abstract no. 18383, "Preparation of cellulose ether powder and apparatus for the preparation" XP002147276 * abstract * & JP 09 076233 A (SHIN ETSU CHEMICAL INDUSTRY CO LTD.) 25 March 1997 (1997-03-25)	1-4	
A	US 2 663 907 A (DOWNING ET AL.) 29 December 1953 (1953-12-29)		

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
C08B
B02C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 October 2000	Mazet, J-F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 30 5260

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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25-10-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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2,663,907

UNITED STATES PATENT OFFICE

2,663,907

CONVERTING FIBROUS CELLULOSE INTO AN EASILY POWDERABLE FORM

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7 Claims. (Cl. 18—48)

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This invention relates to the treatment of cellulose and to its conversion into cellulose derivatives, especially cellulose ethers and esters.

As is well-known cellulose in its naturally occurring forms is almost always fibrous in structure and appearance. The fibres may be long, as in the seed hairs of cotton and in bast fibres such as flax, jute and ramie; or they may be quite short as in some forms of wood pulp, notably pulps obtained from hardwoods, and also some types of cotton linters. As a consequence raw cellulose is supplied in commerce either as a baled and compressed fibrous mass or in the form of compressed fibrous sheets. It is however often desirable to have the cellulose in the form of small particles. Various methods are available for converting compressed baled or sheet cellulose into such a form; the most common method is probably shredding, which converts the compressed cellulose mass of high density into a loose fluffy material of low packing density. In all the known industrial methods the ultimate particles are in the main the original fibres of which the compressed cellulose mass was made up, and it has heretofore been very difficult, if not impossible, to convert fibrous cellulose into a form having a high packing density, as for example a substantially non-fibrous powder.

The present invention provides a method whereby cellulose, for example cotton linters or wood pulp cellulose, can be converted into a flake or powder form of high packing density, showing little or nothing of the original fibrous structure.

We have found that fibrous cellulose can be converted into a form which is easily flaked or powdered by subjecting it to heat and mechanical pressure such that in appearance it partly sinters, but does not char. (While it is necessary that the product shall appear to be partly sintered, the possibility that actual sintering takes place is not excluded.) Preferably the cellulose is at the same time subjected to a shearing action. It is advantageous that the greater part or all of the heat required should be generated within the cellulose by the mechanical deformation to which it is subjected.

In the preferred method of carrying out the invention, the cellulose, for example in the form of a compressed sheet such as a sheet of the type in which wood pulp is commonly supplied and transported, is passed through the nip of one or more pairs of closely set hard-surfaced rolls, the treatment being repeated as may be necessary at least until the cellulose appears to have lost its fibrous form and is in the form of a brittle sheet.

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This brittle sheet may then be subjected to further treatment on the rolls until it is broken down to flakes or powder of the desired degree of fineness, or it may be broken down in some other way, for example in a hammer mill.

The rolls may, for example, be made of or surfaced with steel and are preferably provided with means for cooling or heating them and with means for varying the width of the nip and the relative peripheral speeds of the rolls; thus, rolls of the type frequently used for working rubber may be used with very good results in the present process. The rolls may be kept at or even below room temperature, or they may be heated, e. g. to a temperature between about 50° and 100° C. and especially to about 60°–80° C. Temperatures above about 150° C. are preferably not used. The rolls may be run at the same or different peripheral speeds; preferably the ratio of the peripheral speeds is between about 1.0 and 1.5 or 2.0 and especially about 1.25. The clearance at the nip is preferably less than 0.05 in. and especially less than 0.025 in., a clearance of 0.01 to 0.025 in. usually giving the best results.

The cellulose to be treated need not be given any special treatment before it is passed through the rolls. Thus it may be in a normal air-dry condition. We have, however, found that when the cellulose contains a substantial proportion of moisture, especially above 8%, the product has a somewhat higher molecular weight than when moisture-free cellulose or cellulose containing considerably less than 8% of moisture is treated. Thus before being passed through the rolls the cellulose may be conditioned by steaming, or a fine spray of water may be directed on to the cellulose before it reaches the rolls. If desired, a small proportion of an anti-oxidant, e. g. hydroquinone, may be applied to the cellulose before it enters the rolls, in order still further to conserve the original molecular weight. For example, if the cellulose is sprayed as described above, the spray may contain an anti-oxidant in solution.

The number of passages through the rolls required to convert the cellulose into an easily powderable form will depend partly on the moisture content of the cellulose entering the rolls. As a rule, the lower this moisture content, the more rapidly is the cellulose converted, while with moisture contents above 8%, e. g. 11% or higher, a rather longer treatment is required. Similarly, when dry cellulose or cellulose of low moisture content is treated, it can usually be broken down all the way to a fine powder on the rolls, but when cellulose of a higher moisture content is treated,

and the residue on the sieve was again passed through the rolls until it, too, had been powdered. The two powders were mixed, and the blend had a packing density of about 35 lb./cu. ft.

Example 3

A sheet of purified wood pulp was conditioned to a moisture content of 11.6% and then was passed several times through a pair of unheated rolls set to a clearance of 0.02 in. A hard horn-like sheet was formed which could not easily be reduced to a powder by further treatment on the rolls, but which on being broken up in a bridge Banbury mill gave a powder of packing density above 30 lb./cu. ft.

Example 4

Air-dry cotton linters were passed several times through rolls heated to 65°–80° C. A flake was formed which could easily be powdered, either by further treatment on the rolls or by means of a hammer mill, to give a product of packing density about 35 lb./cu. ft.

Example 5

Carboxymethyl cellulose in a useful powder form was made by the following method from a powdered cellulose of packing density of about 35 lb./cu. ft. obtained as described in Example 2.

17 parts by weight of the powdered cellulose (1 mole) and 32 parts by weight of a 25% aqueous caustic soda solution (2 moles caustic soda) were well mixed in a Werner Pfleiderer mixer. 7 parts by weight of chloroacetic acid (0.75 mole) was then added and mixing continued for 10 minutes; the resulting composition was then allowed to stand with occasional mixing for 4 hours and without any mixing for a further 16 hours. The product was washed with 80% methanol and was then obtained as a white freely flowing powder, completely soluble in hot and cold water, and consisting of 97.15% sodium carboxymethyl cellulose and 2.85% sodium carbonate. Its 2% aqueous solution had a viscosity of 192 cps. and a clarity of 28%.

Example 6

Air-dry powdered cellulose (1 mole) obtained as described in Example 2 was milled for a few minutes in a Werner Pfleiderer mixer with 2.4 moles of caustic soda in 31.5% aqueous solution. 0.7 mole of sodium 2-chloroethane sulphonate was added and mixing was continued for 5 to 10 minutes. During the next 3 hours the mixture was allowed to stand with two 5 minute periods of mixing. It was then transferred to a substantially air-tight container in which it was kept at 50° C. for 27 hours, and at room temperature for another 15 hours. The reaction was conducted under nitrogen throughout. The sulphoethyl cellulose formed was washed with ethanol. It was completely soluble in water and gave a colourless solution of good clarity.

Example 7

Air-dry powdered cellulose (1 mole) obtained as described in Example 2 was introduced into an autoclave at a charging density of 0.08 kgm./litre of reaction space, and stirred for 3 hours with about 4 times its weight of a 60% caustic soda solution at 60° C. under nitrogen. The reactor was then evacuated and about 10 moles of ethyl chloride admitted. The mixture was heated to 125°–130° C. for about 8 hours, stirring all the time. After being cooled the ethyl cellulose formed was still largely in the form of a powder,

and although it showed some tendency to agglomerate and form lumps, these lumps were very friable and easily reconverted into powder. The ethyl cellulose was washed free from alkali with water. It gave a smooth solution in 80/20 benzene/ethanol, and its ethoxyl content was about 44%.

Example 8

Air-dry powdered cellulose obtained in accordance with Example 2 was introduced into an autoclave at a charging density of 0.05 kgm./litre of reaction space, and stirred for 2 hrs. with 1.4 times its weight of a 41.5% caustic soda solution at 25° C. under nitrogen. The reactor was then evacuated and about 16 moles of methyl chloride admitted. The mixture was heated to 70°–95° C. for 2 hours, stirring all the time. The methyl cellulose formed was washed with water at 90° C. until free from salts and then dried at 110° C. It could very easily be broken down into a powder by passing it through a hammer mill. Its methoxyl content was 23.5% and it gave a 2% aqueous solution of good clarity, viscosity 229 cps. at 20° C., and coagulation temperature about 70° C.

Example 9

A powdered cellulose of packing density about 35 lb./cu. ft. produced from cotton linters as described in Example 4 was mixed with half its weight of 93% aqueous acetic acid and allowed to stand for 4 hours at 25° C. It was then fed into an acetylation mixture which had been precooled to 0° C. and which consisted of 3 parts by weight each of acetic acid and acetic anhydride and 14% of sulphuric acid, all based on the weight of the powdered cellulose. After 1¾ hours a clear solution was obtained, the peak temperature reached being 42° C. The solution was then ripened at 25° C. for 48 hours, and the cellulose acetate precipitated by means of dilute acetic acid. It had an acetyl value of 53.3%.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for the treatment of cellulose which is in a visibly fibrous form to render it more easily powdered, which comprises subjecting the visibly fibrous cellulose to the simultaneous action of mechanical pressure and shearing forces applied quickly to the cellulose by the combined forwarding and crushing action of two opposing rotating hard cylindrical surfaces having a temperature below 150° C. and a clearance at the nip less than 0.05 inch, whereby there is generated in the cellulose sufficient heat to raise it to an elevated temperature below its charring temperature, and the visibly fibrous cellulose is changed into a brittle form no longer possessing a fibrous appearance.

2. Process for the treatment of cellulose which is in a visibly fibrous form to render it more easily powdered, which comprises subjecting the visibly fibrous cellulose to the simultaneous action of mechanical pressure and shearing forces applied quickly to the cellulose by the combined forwarding and crushing action of two opposing rotating hard cylindrical surfaces having a temperature below 150° C. and a clearance at the nip less than 0.05 inch, the ratio of the speeds of the said surfaces being between 1:1 and 1:1.5, whereby there is generated in the cellulose sufficient heat to raise it to an elevated temperature below its charring temperature, and the visibly fibrous cellulose is hanged into a brittle form no longer possessing a fibrous appearance.

3. Process according to claim 2, wherein the